

EVOLUTION OF FUEL NITROGEN DURING THE VACUUM THERMAL DEVOLATILIZATION OF COAL

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Introduction

The fate of fuel nitrogen during the combustion or gasification of coal is a matter of practical and fundamental concern. During coal combustion, NO_x is known to form via HCN species released from the nitrogen-containing molecular components of the coal. During gasification processes, the release of nitrogen-containing fused ring compounds in evolved tar species is a matter of environmental concern. Since the thermal decomposition of the parent coal is an initial phase in both combustion and gasification, it is necessary to develop a knowledge of the fate of fuel nitrogen during thermal decomposition.

This study contains results of an investigation of the evolution of fuel nitrogen during the vacuum thermal decomposition of coal. Results are shown for variations with coal characteristics and apparent thermal history. Apparent heating rates of 75 C/sec to 2000 C/sec and final temperatures of 500 C to 1780 C were utilized. A variety of coals were investigated ranging in rank from a lignite to an anthracite.

The results indicate that nitrogen distribution in the volatiles is a sensitive function of the chemical characteristics of the parent coal. This distribution of nitrogen in the light gas, tar and char products of vacuum devolatilized coal is highly dependent on rank of the parent coal. Variations in nitrogen evolution with coal characteristics are most readily apparent in several aspects: (1) the coal nitrogen released with the tar species; (2) the release of nitrogen contained in primary tars as HCN upon secondary thermal decomposition reactions of the primary tars; (3) the retention of nitrogen in the char species.

Experimental Design

Figure 1 represents schematically the apparatus employed to perform the thermal decomposition experiments. The procedure involves placing small samples (20-50 mg) of finely ground coal (-100+325 mesh) between the folds of a fine mesh screen.

Stainless steel is used for final temperatures between 500 C and 1000 C. Tungsten is used for temperatures between 1000 C and 1780 C. The grid is driven to a pre-determined temperature via the preset control circuitry. The apparent heating rate is monitored by a thermocouple bead placed between the folds of the screen.

Light gases are immediately vented through a glass wool filter into a 61 cm long infrared cell in a Fourier Transform Infrared Spectrometer. The cell was calibrated for mixtures of HCN (200, 100, 50 and 25 ppm) diluted in N₂ to a total pressure of 400 torr to avoid the uncertainties of pressure broadening by mixtures. At the end of a devolatilization run the cell and reactor chamber are filled with nitrogen to give a total pressure of 400 torr and simulate the calibration.

The control circuit in this investigation operated a Harrison power supply Model 6269A in the current program mode. In this mode heating rate and final temperature are coupled over the entire final temperature range. The coupling between heating rate and final temperature for the two screen materials can be described by a simple equation of the form $\log(\dot{T}) = mT + B$, where the parameters for each screen are given in Table I. The coupling between heating rate and final temperature is logarithmic in a manner analogous to Newton's law of heating/cooling. For the stainless steel screen the final temperature of 530 C is associated with a heating rate of ~ 100 C/sec while a final temperature of 1000 C is associated with a heating rate of 600 C/sec. The maximum heating rate obtained for the tungsten screen was ~ 2000 C/sec for a final temperature of 1780 C.

Chemical Structure Characteristics of the Coals

The coals examined in this investigation are the same as those previously reported in an investigation of tar yields and characteristics obtained from the devolatilization of the coal.¹ Detailed elemental analyses for the coals are given in Table II. Figure 2 represents the location of the coals on the coalification band as revealed by H/C and O/C values. The position of the Western bituminous coals relative to the Eastern bituminous coals reflects the differences in rank and, indirectly, geologic sources. This figure also reveals the maximum tar yields obtained from these coals. These yields are important characteristics of the devolatilization behavior of a coal as is the variation in tar yield with apparent thermal drive.¹

Figure 3 illustrates the infrared structural characteristics of the coals. Variations in infrared structural characteristics of a coal with its elemental

composition (position on the coalification band) have been previously discussed.^{2,3,4,5} The relationship of the tar yields and temperature sensitivity of tar yields to infrared structural characteristics of the parent coal has also been previously discussed.¹ Proceeding from the low rank side of the coalification band to the high rank side there is an apparent maximum in aliphatic hydrogen absorption ($\sim 3000 - 2750 \text{ cm}^{-1}$) around the location of the Utah bituminous coal ($\text{H/C} = 0.85$, $\text{O/C} = 0.13$). Such an apparent maximum is indirectly observed in the spectra of Fig. 3, normalized with respect to 1 mg of coal in a KBr pellet. It is more directly observable in plots of integrated absorbance versus sample size for each of the coals. The slopes of such plots give apparent extinction of coefficients for each coal. The aliphatic extinction coefficient for the Utah coal is about 24% greater than that of the Pittsburgh seam bituminous coal. Its total hydrogen content is only about 3% greater. The greater apparent aliphatic hydrogen in the Utah bituminous coal reflects not only a difference in the amount of hydrogen present as aliphatic hydrogen, but also the nature and distribution of the molecular species to which the aliphatic hydrogen functional groups are attached.⁶

In proceeding through the coalification band it is also noted that the resolution of the aromatic hydrogen peaks ($\sim 3040 \text{ cm}^{-1}$, $680-920 \text{ cm}^{-1}$) increases with rank. This increase in resolution is reflected in the apparent aromatic hydrogen absorption coefficients of the coals. The integrated area absorption coefficients for aromatic hydrogen generally increase with rank for these coals. If the strength of the bands associated with aromatic hydrogen absorption is an indication of the aromaticity of the coal, then the spectra of these coals indicate a consistent increase in aromaticity with rank as reflected by the position on the coalification band diagram (Fig. 2).

These structural considerations are important because they lead to general understanding of the relationship between chemical structural characteristics of a coal and its primary devolatilization behavior. A previous report demonstrated that the influence of chemical structure on devolatilization for subbituminous and bituminous coals is most clearly reflected in the primary (vacuum, disperse phase, small particle size) tar yields and tar characteristics.¹ This report demonstrates that the nitrogen distribution in the primary volatiles and char residual can also be related to structural characteristics of the parent coal.

Nitrogen Distribution in the Devolatilization Products Coal Nitrogen in the Char, Tar, Light Gas Species

Typical mass fraction distributions of the coal nitrogen in the devolatilization products are listed in Table III. Typical distributions are illustrated in Figs. 4-7. The data indicates that little (< 5%) of the coal nitrogen is evolved as HCN in those runs characterized by final temperatures of 700 C and below. In the 500 C to 700 C final temperature runs, most of the volatile nitrogen is in the tar species. As the thermal drive is increased (final temperatures ~ 700 C to ~ 950 C) HCN becomes a greater component in the volatiles nitrogen. The temperature dependence of the HCN evolution in this temperature range is coal dependent. The subbituminous and Western bituminous coals, for example, give sharper increases in HCN evolution with respect to final temperature than the Pittsburgh bituminous or Alabama bituminous.

For all of the samples examined except the anthracite, more of the coal nitrogen is evolved as an element of the tar species than as HCN in the < 1000 C runs. In the range of conditions, the retention of coal nitrogen in the char residue is similar for the subbituminous and Western bituminous coals. The fraction of coal nitrogen retained in the char is approximately the same for the same final temperature. The temperature dependent nitrogen retention in the chars of the Eastern bituminous coals (high volatile A Pittsburgh seam, Alabama medium volatile) is appreciably different than those of the subbituminous and Western bituminous coals. The chars of the Pittsburgh seam show less nitrogen variations with final temperature. The medium volatile bituminous chars show nitrogen variation with temperature similar to that of the Western bituminous but at higher levels of mass fraction retention.

Mass Fractions of Coal Nitrogen in Tar

All of the coals show substantial increases in nitrogen evolved as HCN for final temperatures above 950 C. A portion of this increase is the result of secondary cracking reactions of primary tar vapors under the conditions of increased thermal drive. As noted above, a previous study¹ on tar yields revealed that tar yields can be substantially modified by increasing the heating rate of the coal. Reduction in the tar yields by an increase in thermal drive results in a corresponding reduction in the coal nitrogen evolved in the tar. Cracking of the nitrogen - containing tar species results in the evolution of the nitrogen as HCN. The relationship between the coal nitrogen and the evolved tar species is illustrated in Figs. 8-10.

Figure 8 shows the fractions of Utah bituminous coal mass and coal nitrogen evolved as tar and as an element of the tar species for various final temperatures. Figure 9 shows plots of the mass fraction of coal evolved as tar versus the mass fraction of coal nitrogen evolved as tar, irrespective of thermal drive conditions. As the tar species are reduced by increasing the thermal drive, nitrogen is released as HCN from the tar cracking process.

Mass Fractions as CHAR

Figures 10 and 11 plot the mass fraction of the coal evolved as char versus the mass fraction of the coal nitrogen evolved as char nitrogen. As with the tar plots, upon elimination of the thermal history parameter, there is an obvious similarity in the nitrogen evolution of the subbituminous and bituminous coals. The plots indicate that the main phase of the devolatilization process is characterized by nitrogen retention in the char in proportion to the fraction of coal mass evolved as char. At mass fractions of char greater than ~ 0.5 (characterized by runs of 950 C final temperature and less) all of the chars lost retained nitrogen at a rate much greater than additional mass loss.

Phenomenological Description of Nitrogen Evolution

A phenomenological description of the evolution of coal nitrogen during vacuum devolatilization emerges from the investigation. For final temperatures of 950 C and less and apparent heating rates of 600 C/sec and less, the tar and char species generally contain 0.7 or more of the coal nitrogen. In this range of conditions, tar removes coal nitrogen in proportion to the mass fraction of coal evolved as tar. Char retains nitrogen in proportion to the mass fraction of coal evolved as char. The balance of the coal nitrogen evolves predominantly as HCN. Small but observable amounts of NH_3 are produced at low final temperatures. More NH_3 appears to be formed from low rank coals.

The distribution of the coal nitrogen in the tar, char or light gases produced during devolatilization is dependent on the rank of the parent coal in a manner analogous to the distribution of coal mass as tar, char or light gases. An increase in the fraction of volatiles evolved as tar with increase in rank results in a proportionate increase in nitrogen evolution as an element of the tar species. A decrease in tar yield with increase in thermal drive, results in a proportionate decrease in coal nitrogen evolved as tar. As the tar yield decreases, the tar nitrogen is evolved as HCN. Higher rank coals appear to produce tars more thermally stable than lower rank coals (See Reference 1).

For final temperatures greater than 950 C and heating rates in excess of 600 C/sec, Western bituminous and subbituminous coals display tar yield reductions as great as 50-60% of the maximum tar yield. The coal nitrogen evolved as tar is proportionately reduced. At volatile yields greater than ~ 0.5 of the parent coal the primary form of nitrogen evolution from the char is HCN. At these levels of conversion little increase in total volatiles by mass is observed while substantial reductions in char nitrogen levels are observed.

Relationship of Nitrogen Devolatilization Behavior to Coal Structural Characteristics, Structural Models

The chemical nature of the nitrogen distribution in the mix of molecular species present in the parent coal is indicated by the following phenomenological observations: (1) non-preferential evolution of coal nitrogen as char, tar or light gas during the devolatilization process; (2) the nitrogen distribution in the devolatilization products (tar, char, light gas) varies with rank and thermal drive as does the distribution of coal mass as char, tar and light gas; (3) HCN is the dominant nitrogen-containing light gas observed in rapid-heating; disperse phase devolatilization.

In the context of related investigations and a previous report on tar yields/characteristics, the observations indicate: (1) nitrogen is uniformly distributed throughout the mix of molecular species present in the parent coal, irrespective of rank; (2) the primary type of nitrogen-bonding present in the parent coal is as a heteroatom in an aromatic ring system, i.e., pyridine-type; (3) variations with rank in the nitrogen distributions in the devolatilization products can be understood on the basis of a shift with rank in a condensation frequency function (the distribution of molecular species as characterized by the number of fused rings/structure).

This devolatilization study as well as others indicate^{7,8} that HCN is the principal nitrogen-containing light gas evolved during disperse phase, rapid-heating coal devolatilization. Studies performed by Houser,⁹ et. al. and Axworthy,¹⁰ et. al. indicate HCN is the principal light gas evolved from the thermal decomposition of pyridine-type nitrogen compounds. In addition, recent studies performed by Deno, et. al.¹¹ indicate that the nitrogen present in the parent coal is found as an heteroatom in aromatic ring structures. Taking into account the known highly aromatic nature of coals, the data of this study indicate that the primary form of nitrogen appears to be as a heteroatom in aromatic ring structures.

As noted in an earlier report,¹ distinguishing features of the devolatilization behavior of a coal are its maximum tar yield and the sensitivity of tar yield to the conditions of thermal drive. It was shown, for example, that the Pittsburgh seam bituminous coal gave a maximum tar yield ~ 40% greater than the Utah bituminous coal, ~ 50% greater than either the Colorado bituminous or Alabama bituminous coals, ~ 85% greater than the two subbituminous coals. Only a small fraction of the lignite was evolved as tar and the anthracite gave only light gases. The Pittsburgh seam coal (HVA) and Alabama bituminous coal (MVB) gave tar yields which were relatively insensitive to changes in thermal drive by comparison to the Western bituminous and subbituminous coals. Total vacuum volatile yields do not vary significantly with rank until coals with characteristics of the medium volatile bituminous coal. This report indicates that the nitrogen distribution in the devolatilization products reflects these patterns.

Thus moving along the coalification band from the low rank to the high rank side, the tar yield becomes a greater fraction of the total volatiles evolved and the primary tars formed appear to be more thermally stable. Correspondingly, more of the parent coal nitrogen is evolved as tar and is retained by the thermally stable tars of these coals.

The devolatilization data, indicate that an increase in a condensation index (shift to a higher average number of the frequency function describing #fused rings/molecular species) and aromaticity of coal with position on the coalification band provides a reasonable explanation of changes in behavior with rank. The chemical nature of the nitrogen distribution in the parent coal forces the coal nitrogen devolatilization behavior to reflect the coal mass devolatilization behavior.

The variation in devolatilization behavior with rank appears to support some earlier attempts to develop a model of coal constitution based on the average number of fused rings in a molecular unit (lamella) of the coal. A model such as suggested by Ayre and Essenhight¹² and latter modified by Scaroni and Essenhight¹³ appears able to provide a reasonable explanation of behavior with some qualifications. The data of this study indicate a change in devolatilization behavior with respect to total yield at a carbon content lower than 90%. The data also indicates a change in devolatilization behavior with respect to the yields and characteristics much lower than 90%. It is believed that a statistical function of the type described above showing a pronounced shift in characteristics in the 82-85% carbon level would more adequately reflect behavior observed in these studies.

The devolatilization data of this study and the previous tar study indicate that coal does behave as if it devolatilizes in two stages. The main stage (mass fraction conversions of ~ .4-.5) of volatile evolution requires relatively low final temperatures and is followed by a second stage of volatile evolution requiring temperatures in excess of 1000 C for appreciable rates. The coal nitrogen does evolve as if it were contained in two components. The two-component hypothesis of coal constitution was first noted by Clark and Wheeler¹⁴ and later emphasized by Essenhigh and Howard¹⁵ to explain devolatilization behavior.

However, rather than identifying the easily evolved volatile matter as being generated by the weakly bonded amorphous material associated with stacked ring structures, the data suggest the easily evolved nitrogen to be associated with ring structures susceptible to thermal cracking and/or volatilization at temperatures of 950 C or below. Variations with rank in easily evolved nitrogen expelled as tar or HCN reflect variations in the ring size distribution function with rank characteristics. The Pittsburgh seam bituminous coal evolves more coal nitrogen as tar than the Utah bituminous coal because its parent nitrogen is contained in ring structures more thermally stable, that is, of greater degree of ring condensation and having fewer associated functional groups. For the same reason, the Alabama bituminous (medium volatile) coal initially expels most of its nitrogen as tar. The Alabama bituminous yields less total volatiles than the high volatile bituminous coals because a greater fraction of its nitrogen is associated with non-volatile ring structures. That is it contains a large fraction of structures too large to be volatilized before char-incorporating secondary reactions "polymerize" the species in the char matrix.

This study on nitrogen evolution and the previous study dealing with tar yields and characteristics obtained from a variety of coals indicates:

1. In vacuum devolatilization conditions, coal behaves as if it contains two volatile components, as previously noted.
2. Lignite to high volatile bituminous coals can be differentiated with respect to devolatilization yields, primarily tar yield and characteristics.
3. Coal nitrogen distribution in the volatile products for subbituminous coals and higher ranks reflects the coal mass distribution in the volatile products.

4. Coal nitrogen for subbituminous and higher rank coals behaves as if it were incorporated as an heteroatom in the aromatic ring system of the parent coal.
5. As previously noted, variations in devolatilization behavior with rank appear to reflect a variation in the degree of ring condensation present in the coal matrix.
6. Variations in devolatilization behavior (more specifically, tar and nitrogen evolution) with rank reflect a shift in the characteristics of a ring-size distribution function with rank.

TABLE I

COUPLING BETWEEN FINAL TEMPERATURE AND HEATING RATE

<u>Screen Material</u>	<u>m</u>	<u>b</u>	<u>T Range, °C</u>
Stainless steel	1.96×10^{-3}	0.92	530 - 950
Tungsten	6.50×10^{-4}	2.16	1000 - 1750

REFERENCES

1. Freihaut, J. D. and Seery, D. J., Amer. Chem. Soc. Div. of Fuel Chem. Preprints, 26, No. 2, 133 (1981).
2. Brown, J. K. and Hirsch, P. B., Nature, 175, 229 (1955).
3. Fujii, S., Osawa, Y., and Sugimura, H., Fuel, 49, 68 (1970).
4. Solomon, P. R., Amer. Chem. Soc. Div. of Fuel Chem. Preprints, 24, No. 3, 184 (1979) and Advances in Chemistry (to be published).
5. Painter, P. C., et. al. Applied Spectroscopy (to be published).
6. Bellamy, L. J. The Infrared Spectra of Complex Molecules, John Wiley & Sons, New York (1975).
7. Pohl, J. H. and Sarofim, A. F., Sixteenth Symp (Intern) on Combustion, The Combustion Institute, Pittsburgh, 491 (1979).
8. Blair, D. W., Wendt, J. D. L., and Bartok, N., Sixteenth Symp (Intern) on Combustion, The Combustion Institute, Pittsburgh, 475 (1977).
9. Houser, T. J., et. al., Int. Jr. of Chem. Kinetics, XII, 555 (1980).
10. Axworthy, A.E., et. al., Fuel, 57, 29 (1978).
11. Deno, N. C., Pennsylvania State U., Dept. of Chem, Private Communication.
12. Ayre, J. L. and Essenhigh, R. H. Sheffield Univ. Fuel Soc. Jr., 8, 44 (1957).
13. Scaroni, A. W. and Essenhigh, R. H., Amer. Chem. Soc. Div. of Fuel Chem.. Preprints, 23, No. 4, 124 (1978).
14. Clark, A. H. and Wheeler, R. V., Trans. Chem. Soc., 103, 1754 (1913).
15. Essenhigh, R. H. and Howard, J. B., The Pennsylvania State U., Studies, 31 (1971).

TABLE II

ELEMENTAL ANALYSIS (DMF)

	Mon Lig(L)	WY Sub(S1)	WY Sub(S2)	Utah Bit(UB)	Col Bit(CB)	Pitt Bit(PB)	Ala Bit(AB)	Anth. (AN)
C	0.6827	0.7540	0.7550	0.7818	0.8100	0.8197	0.8497	0.9369
H	0.0457	0.0490	0.0517	0.0552	0.0553	0.0536	0.0463	0.0259
O	0.2547	0.1807	0.1699	0.1386	0.1119	0.0936	0.0818	0.0189
N	0.0102	0.0128	0.0171	0.0169	0.0163	0.0142	0.0173	0.0108
S _O	0.0067	0.0035	0.0063	0.0076	0.0064	0.0109	0.0052	0.0072
H/C	0.803	0.780	0.822	0.847	0.819	0.785	0.654	0.332
O/C	0.280	0.180	0.169	0.133	0.104	0.086	0.072	0.015

TABLE III - 1

NITROGEN DISTRIBUTIONS IN DEVOLATILIZATION PRODUCTS

Subbituminous 2 (SUB B)

$T_f(^{\circ}\text{C})$	$f^{\text{N}}_{\text{CHAR}}$	$f^{\text{N}}_{\text{tar}}$	$f^{\text{N}}_{\text{HCN}}$	Σf^{N}
520	0.99	0.05	---	1.04
600	0.76	0.24	0.01	1.01
745	0.67	0.19	0.10	0.96
820	0.63	0.28	0.17	1.00
890	0.57	0.22	0.21	1.00
945	0.57	0.12	0.20	0.89
950	0.53	0.11	0.30	0.94
1040	0.48	0.17	0.30	0.95
1090	0.40	0.14	0.40	0.94
1160	0.31	0.07	0.63	1.01
1240	0.28	0.06	0.65	0.99
1365	0.17	0.06	0.66	0.89
1390	0.08	0.04	0.61	0.73
1600	0.10	0.04	0.54	0.68
1700	0.08	0.04	0.92	1.03
1780	---	0.03	0.87	0.90

TABLE III - 2

NITROGEN DISTRIBUTIONS IN DEVOLATILIZATION PRODUCTS

Utah Bituminous (HVB)

<u>T_f(°C)</u>	<u>f^N_{CHAR}</u>	<u>f^N_{tar}</u>	<u>f^N_{HCN}</u>	<u>Σf^N</u>
530	0.81	0.04	0.01	0.86
595	0.66	0.22	0.01	0.89
745	0.58	0.26	0.08	0.92
790	0.57	0.27	0.09	0.93
880	0.49	0.25	0.17	0.91
915	0.48	0.24	0.17	0.89
935	0.51	0.30	0.13	0.94
1020	0.42	0.29	0.16	0.87
1090	0.40	0.24	0.25	0.89
1160	0.44	0.22	0.38	1.04
1240	0.30	0.21	0.51	1.02
1390	0.20	---	0.61	0.81
1600	0.20	0.10	0.67	0.97
1700	0.13	0.06	0.72	0.91
1780	0.10	0.05	0.96	1.11

TABLE III - 3

NITROGEN DISTRIBUTIONS IN DEVOLATILIZATION PRODUCTS

Pittsburgh Bituminous (HVA)

$T_f(^{\circ}\text{C})$	$f_{\text{CHAR}}^{\text{N}}$	$f_{\text{tar}}^{\text{N}}$	$f_{\text{HCN}}^{\text{N}}$	Σf^{N}
565	0.61	0.49	0.01	1.11
585	0.61	0.38	0.01	1.00
618	0.58	0.45	0.00	1.03
735	0.55	0.41	0.05	1.01
745	0.59	0.41	0.05	1.05
775	0.52	0.41	0.06	0.99
830	0.53	0.39	0.09	1.01
855	0.54	0.43	0.10	1.07
915	0.46	0.36	0.10	0.96
935	0.55	0.36	0.08	1.09
1040	0.44	0.40	0.10	0.94
1090	0.50	0.60	0.12	1.21
1107	0.41	0.40	0.24	1.04
1125	0.39	0.39	0.17	0.95
1165	0.46	0.43	0.22	1.11
1220	0.32	0.28	0.20	0.80
1220	0.39	0.36	0.33	1.08
1300	0.29	0.54	0.30	1.13
1450	0.33	0.19	0.33	0.85
1450	0.26	0.30	0.37	0.93
1700	0.04	---	0.43	0.47
1780	0.06	0.15	0.28	0.49

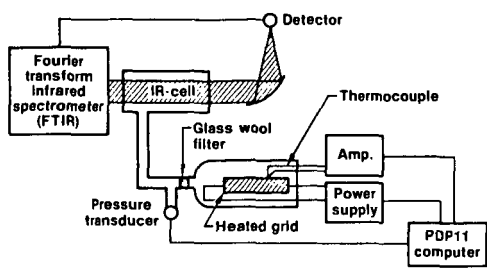


Fig. 1 Heated Grid Apparatus

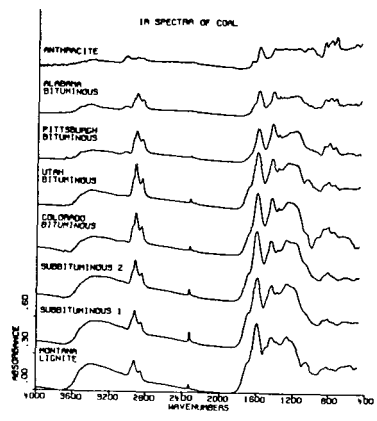


Fig. 3 IR Spectra of Coals

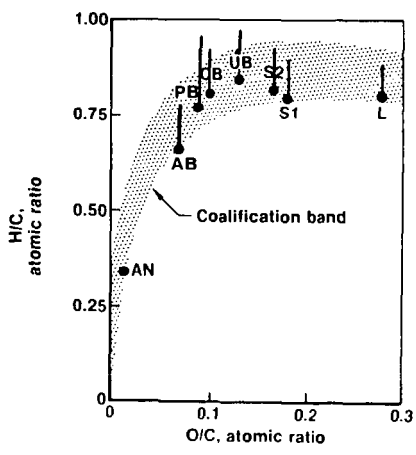


Fig. 2 Coal Band Location

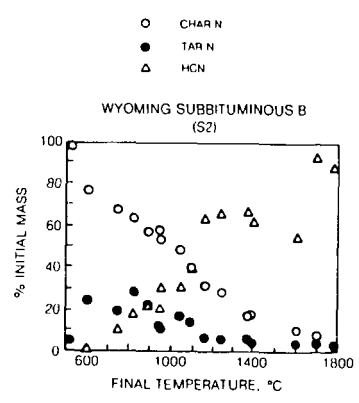


Fig. 4 Nitrogen Distribution: Subbituminous Coal

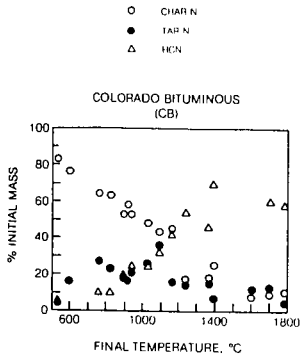


Fig. 5 Nitrogen Distribution: Colorado Bituminous Coal

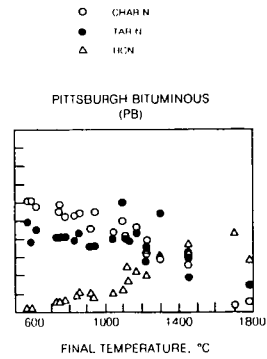


Fig. 7 Nitrogen Distribution in Pittsburgh Bituminous Coal Devolatilization Products

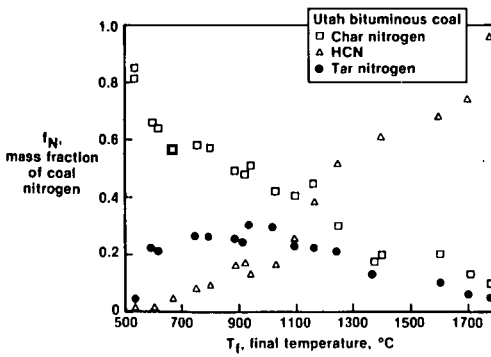


Fig. 6 Nitrogen Distribution: Utah Bituminous Coal

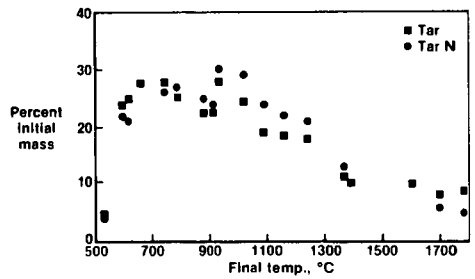


Fig. 8 Mass Fraction of Coal Mass and Coal Nitrogen vs. Final Temperature for Utah Bituminous Coal

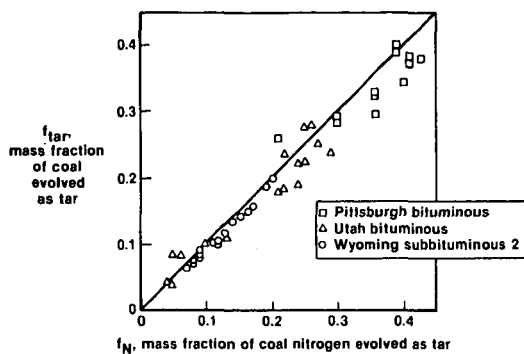


Fig. 9 Mass Fraction of Coal as Tar vs. Fraction of Coal Nitrogen as Tar

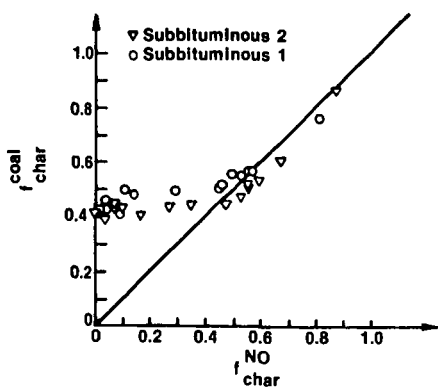


Fig. 10 Mass Fraction of Coal as Char vs. Fraction of Coal Nitrogen as Char

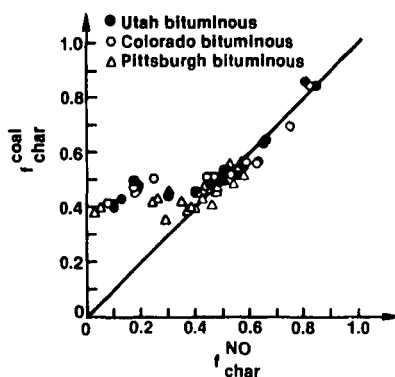


Fig. 11 Mass Fraction of Coal as Char vs. Fraction of Coal Nitrogen as Char